

AN AUTOMATIC (OR SEMI-AUTOMATIC) APPARATUS FOR THE DETERMINATION OF MELTING CURVES

by

W. M. SMIT AND G. KATHEMAN

Netherlands Central Institute for Physicochemical Constants, Utrecht (The Netherlands)

INTRODUCTION

The apparatus to be described is a "thin film" apparatus operating automatically within a range of about 0.2°C and a temperature sensitivity of about 0.001°C . Larger temperature ranges may be investigated, either fully automatically with a temperature sensitivity which is inversely proportional to the temperature range to be investigated, or semi-automatically by dividing the temperature range into parts of about 0.2°C . In the latter case the temperature sensitivity remains 0.001°C .

The calorimetric part of the apparatus is essentially the same as that of the hand-operated apparatus, mentioned in previous papers¹. Since up to now we have not given any account of the principles on which the "calorimeter" is based, it seemed useful to begin by doing so and then to describe an adapted system of controlling and recording.

Principle of the apparatus

The "calorimeter" consists of a cylindrical metal block containing a coaxial cylindrical air space. The substance to be investigated is contained in an annular space between the "thermometer" and the inside wall of the measuring vessel. The axis of the measuring vessel coincides with the axis of the block.

The metal block is heated at such a rate that its temperature differs constantly, by a distinct number of degrees, from the temperature indicated by the central thermometer. Consequently the flow of heat from the wall of the block to the measuring vessel (or reverse) is almost constant.

This method as such for obtaining a constant heat supply has already been applied by THOMAS AND PARKS².

In the apparatus described here the substance is spread in a single thin layer and no stirring is applied. In the hand-operated apparatus the temperatures of the block and the measuring vessel are indicated by mercury thermometers (A special type of *small* Beckmann thermometer, subdivided in 0.05°C , rendered good service.)

In the automatic apparatus resistance thermometers have been applied. The resistance of the inner thermometer is recorded as a function of time, whereas the controller for heating the block operates on the difference of the specific resistance of the outer and inner thermometer.

THE CALORIMETER

Description of the calorimeter

The calorimeter (see Fig. 1) consists of an aluminium cylindrical block (5) with a central bore, closed by a forced-in aluminium cover. A hole in this cover permits introduction of the glass measuring vessel (6). When in use the measuring vessel contains a

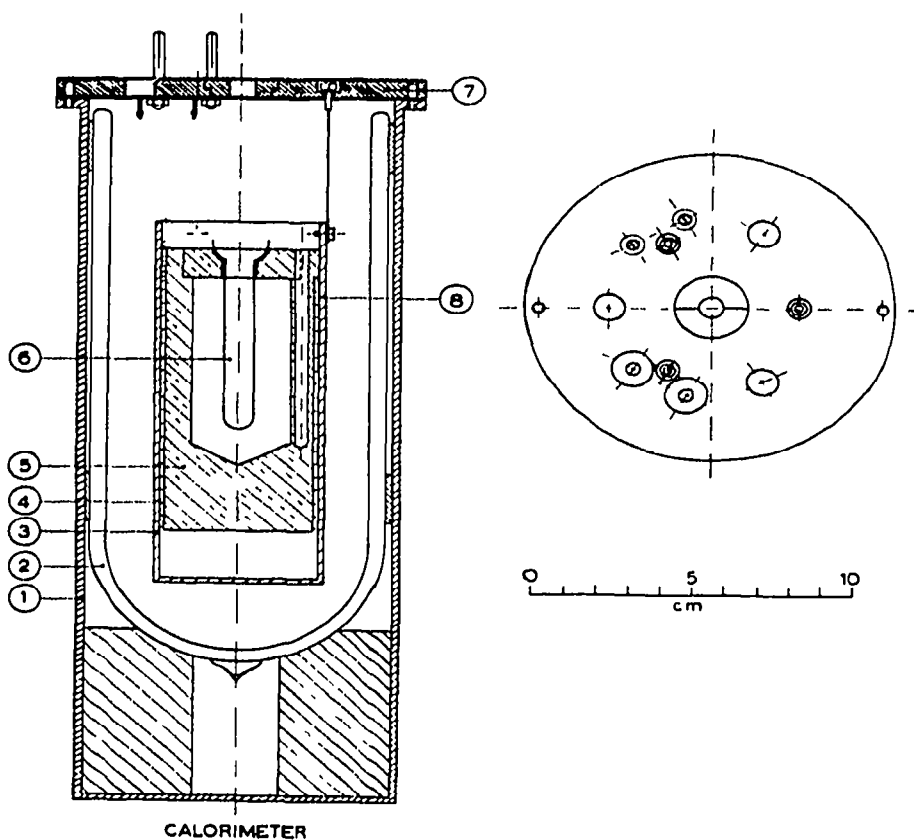


Fig. 1

(central) thermometer. A second (outer) thermometer may be inserted in a thermometer well (8). The block (5) is surrounded by a heating element (4) (400 ohms); this consists of a heating coil of constantan strip insulated by glass wool. The coil is enclosed between two single layers of thin asbestos paper. The block, together with the heating element, is contained in a closely fitting cylindrical aluminium jacket (3). It is suspended to the large asbestos cement cover (7) by means of thin stainless steel rods. The cover (7) rests on the outer jacket (1) containing the Dewar flask (2).

Dimensions of the measuring vessel

The considerations on which the dimensions of the measuring vessel, the layer of substance, and the thermometer, were based are given in the accompanying paper³.

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Dimensions of the block

The outer dimensions of the measuring vessel having been decided on, the optimal dimensions of the block were estimated on the basis of the following considerations.

As is obvious, the heat supplied to the measuring vessel increases when the temperature difference between the block and the measuring vessel is increased. In order to obtain a reliable heating curve the heat supply, and thus the temperature difference, should be low. On the other hand, a low temperature difference involves great demands on the sensitivity of the system controlling this temperature difference. The accuracy aimed at, combined with the sensitivity of the controlling system set a lower limit for the allowable temperature difference. Therefore, it is worthwhile to investigate at what dimensions of the metal block the heat supply to the measuring vessel is minimal at a given temperature difference.

Heat is transferred from the inside wall of the block to the measuring vessel by means of conduction and radiation (Since the temperature differences occurring are relatively small, convection is neglected)

As the length of the cylindrical bodies amounts to several times their respective diameters it is permissible to estimate the heat transfer to the measuring vessel by applying the laws obtaining to coaxial cylindrical bodies of infinite length.

The heat (Q) transferred per unit time and per unit length to the inner cylinder of a system of two coaxial cylinders separated by an annular air space amounts to

$$Q = \frac{2\pi\lambda(T_2 - T_1)}{\ln r_2/r_1} + 2\pi r_1 \left[\left(\frac{T_2}{100} \right)^4 - \left(\frac{T_1}{100} \right)^4 \right] C \text{ cal/sec cm}^* \quad (1)$$

where the first term of the right-hand member represents the heat transferred by conduction and the second term represents the contribution of radiation, and

$$\frac{1}{C} = \frac{1}{C_1} + \frac{r_1}{r_2} \left(\frac{1}{C_2} - \frac{1}{C_s} \right)$$

Further λ is the heat conductivity of air

r_1 is the outer radius of the inner cylinder (measuring vessel)

r_2 is the inner radius of the outer cylinder (metal block)

T_1 absolute temperature at r_1

T_2 absolute temperature at r_2

C_s is the black body emissivity

C_1 is the emissivity of the surface of the inner cylinder

C_2 is the emissivity of the inner surface of the outer cylinder

Discussion of equation (1)

As is clear from equation (1), the heat transferred to the measuring vessel depends on quite a number of factors, viz., C_1 , C_2 , λ , r_1 , r_2 , T_1 and T_2

C_1 represents the emissivity of the outer wall of the measuring vessel. A glass measuring vessel is easy to make and permits inspection of the sample. The high emissivity of glass is a drawback that may be compensated to a large extent when the emissivity of the block (C_2) is low. It was therefore decided to choose a glass measuring vessel, thus fixing the value of C_1 at 0.94 C_s , which is the value obtaining for glass.

* See e.g. A. SCHACK, *Der Industrielle Wärmeübergang*, Düsseldorf, 1953
W. H. Mc ADAMS, *Heat Transmission*, New York, 1942

The influence of the remaining factors is illustrated by a series of graphs (see Figs. 2, 3, 4, 5)

Fig. 2 shows the flow of heat (Q) as a function of r_2 at different values of C_2 ($r_1 = 0.4$ cm; $T_1 = 573^\circ\text{C}$; $T_2 = 574^\circ\text{C}$, and $\lambda = 10^{-4}$ cal/cm.sec degree.) It appears that a low value of C_2 is preferable.

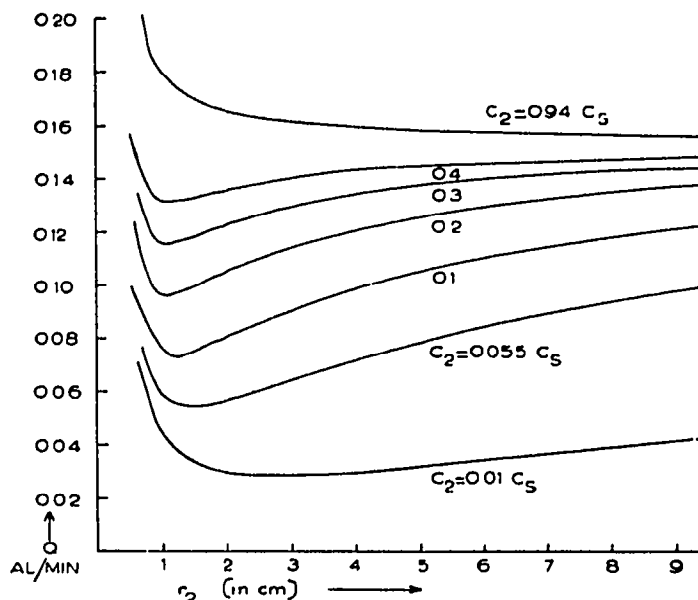


Fig. 2 Flow of heat as function of inner radius of calorimeter at different emissivities

Polished surfaces of several metals have a low emissivity. However, the emissivity of these surfaces soon increases when exposed to the atmosphere of a laboratory at elevated temperatures, with the exception of surfaces of gold or non-polished aluminium. Non-polished aluminium has a fairly low emissivity, *viz.* $C_2 = 0.055 C_s$. Further, aluminium has a high temperature conductivity and is inexpensive. Accordingly, the block was made of aluminium, thus fixing the value of C_2 at about $0.055 C_s$. The curve of Fig. 2 obtaining for $C_2 = 0.055 C_s$ shows a minimum at $r_2 = 1.5$ cm.

Fig. 3 shows the flow of heat (Q) as a function of r_2 at different temperatures. The curves of this graph hold good for $C_1 = 0.94 C_s$, $C_2 = 0.055 C_s$; $r_1 = 0.4$ cm and $T_2 - T_1 = 1^\circ\text{C}$, λ is a temperature function varying from $0.5 \cdot 10^{-4}$ at 273°K to 10^{-4} cal/cm.sec degree at 573°K . (The applicable values of λ have been derived from Landolt-Bornstein, Physikalisch-Chemische Tabelle.)

All the curves of Fig. 3 show a minimum. The minima have been connected by a dotted line. It appears that the minima at low temperatures are far less pronounced than those at high temperatures. The value of Q at $r_2 = 1.5$ cm differs only slightly from the minimal value obtainable at a certain temperature within the range of 173 – 573°K . Therefore a value of $r_2 = 1.5$ cm may be preferable. However, it must be remembered that Q is also a function of r_1 (see Fig. 5).

Fig. 4 shows Q as a function of r_2 at different values of $T_2 - T_1$. ($C_2 = 0.055 C_s$; $r_1 = 0.4$ cm, $T_1 = 573^\circ\text{K}$; $\lambda = 10^{-4}$ cal/cm. sec degree.) It appears that the minimum in the

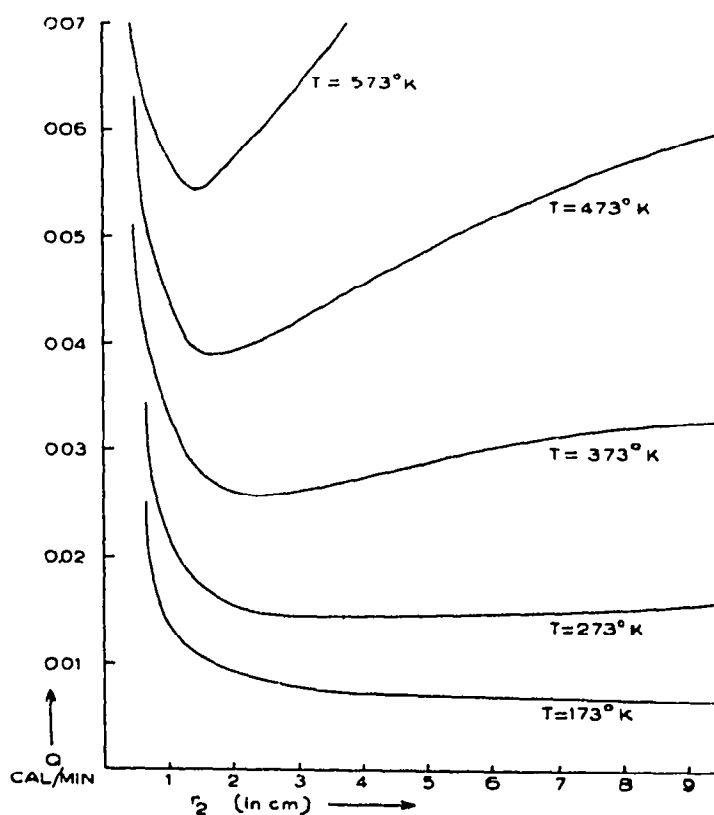


Fig. 3. Flow of heat at different temperature as function of inner radius

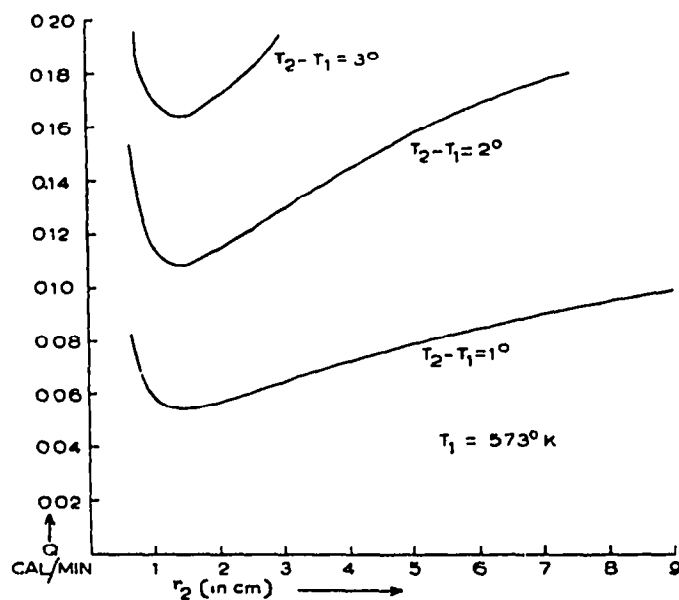


Fig. 4 Flow of heat at different thermal heads as function of inner radius.

(Q, r) curves is independent of $T_2 - T_1$. Further, Q is approximately proportional to $T_2 - T_1$, at least when $(T_2 - T_1) < 3^\circ\text{C}$

Fig 5 shows Q as a function of r_2 at different values of the outside diameter (r_1) of the measuring vessel ($C_2 = 0.055 C_s$, $T_1 = 573^\circ\text{C}$, $T_2 = 574^\circ\text{C}$, $\lambda = 10^4$ cal/cm. sec degree.)

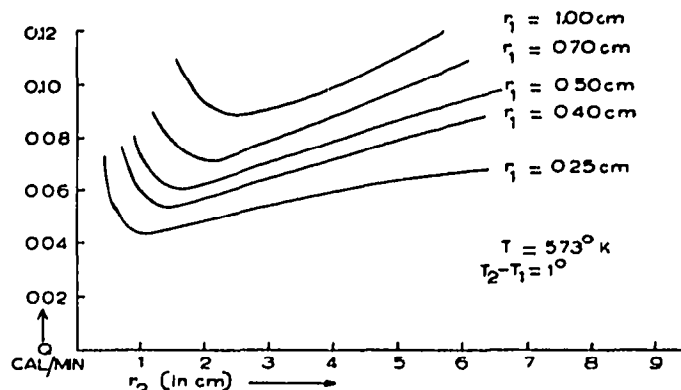


Fig 5 Flow of heat as function of inner radius at different radii of the measuring vessel

It appears that the minimum in the (Q, r_2) curves shifts to higher values of r_2 when r_1 increases. Therefore the inner radius of the block should be adapted to the outer radius of the measuring vessel. In its turn the outer radius of the measuring vessel depends on the radius of the thermometer (see preceding paper). The radii of suitable mercury thermometers vary from about 0.2 to 0.4 cm. (As will be shown, it is possible to construct resistance thermometers with comparable radii.) This range of thermometer radii corresponds to a range of vessel radii from about 0.25 to 0.5 cm. Within this range of vessel radii the value of r_2 at which Q is minimal varies only from 1.3 to 1.7 cm. Therefore an inside radius (r_2) of the block equal to 1.5 cm has been chosen, this being a mean value permitting the use of commercially available thermometers and ensuring a low heat transfer within a very wide range of temperature.

Experimental checks on equation (1)

Experimental checks on equation (1) have been carried out with aluminium blocks having inner radii of 1.0 and 1.5 cm, respectively. Further, all-glass apparatuses ($C_2 = 0.94 C_s$) with inside radii r_2 of 0.9, 1.1, 1.5 and 1.8 cm, respectively, have been investigated. The flow of heat (per unit length of the measuring vessel) during each experiment has been determined by measuring the time required to melt a known amount of substance (per unit length) having a known heat of fusion. The experiments have been carried out at $T_1 = 321^\circ\text{K}$ or 425°K , and values of $T_1 - T_2$ equal to 2.0, 2.2, 2.5 and 3°C have been applied. The difference between the flow of heat actually found in this series of ten experiments never differed in any of the cases more than 10% from the value calculated.

MEASURING AND CONTROLLING PARTS

Temperature detection system

Electrical detection of temperature and temperature differences may be carried out either with thermocouples or with resistance thermometers. In the case to be discussed here the accuracy aimed at is 0.001°C corresponding with an e.m.f. of $5 \cdot 10^{-8}$ V for a copper-constantan couple.

It is very difficult to build a both stable and linear D.C. amplifier with a noise level as low as $5 \cdot 10^{-8}$ V. According to our experience it is possible to build a linear D.C. amplifier stable within 10^{-6} V without using selected amplifier tubes. Accepting the value of 10^{-6} V as a reasonable lower limit involves the use of a 20-fold thermocouple to obtain an accuracy of 0.001°C . A 20-fold thermocouple, however, if applied in our calorimeter, would upset the whole system of heat transfer because of the relatively large heat conductivity of such a thermopile. Other drawbacks of a thermopile are its relatively large volume and the necessity of a reference point constant within 0.001°C .

Resistance thermometers seem to be more suitable. N.T.C. resistors (thermistors) were rejected because of their relatively small temperature range, instability at temperatures above 100°C , and complicated temperature function. The requirements to be met by a resistance thermometer suitable for our purposes are: high temperature coefficient, high resistance and small volume.

It appeared that these requirements could be met with by selfmade resistance thermometers with a resistance wire of tungsten or platinum.

The resistance thermometer

The total resistance required has been calculated in the following way. Suppose the resistance thermometer to be part of a Wheatstone bridge consisting of four almost equal resistors. Then the bridge signal varies with $\frac{1}{4}\alpha V$ volts per degree, when V is the voltage applied to the bridge and α is the temperature coefficient of the resistance thermometer. Because of the accuracy aimed at and the noise level of the amplifier, the variation of the bridge signal should be larger than 10^{-3} volt/degree. Since α equals about 0.4% per degree for tungsten or platinum the voltage fed to the bridge should be at least equal to one volt, causing a voltage over the resistance thermometer of about 0.5 volts. Suppose the bridge to be fed with direct current and the resistance of the thermometer to be R ohms. Then the heat developed by the thermometer amounts to $(0.25 R \times 0.24 \text{ cal/sec})$. The total heat required for heating the measuring vessel and its contents amounts to about 10^{-3} cal/sec not allowing more than 10% of the total heat required to be developed by the resistance thermometer. A value for R of at least 600 ohms results.

The size of the sensitive part of the resistance thermometer should preferably be comparable with the bulb of a common mercury thermometer.

It appeared that 5-watt glow lamps contained a coil of tungsten wire having a resistance of about 600 ohms at room temperature. The length of the coil is about 9 cm and its diameter is only 0.1 mm. It proved to be possible to mount such a coil in a helix etched in a small glass tube and to seal the whole in a second thin-walled glass tube of a slightly larger diameter. The ends of the tungsten coil were silver-soldered to platinum leads through the outer glass tube. We also constructed platinum resistance thermometers of comparable size and resistance in almost the same way. Platinum

wire of a diameter of 0.015 mm was used. It was wound bifilarly around a glass tube having an etched helix of about three turns per mm. The temperature-sensitive part of these thermometers has a diameter of about 6.5 mm and a length of about 25 mm. The resistance at room temperature is about 600 ohms.

Circuits for measuring and controlling

The circuits for measuring and controlling start with two combined Wheatstone bridges shown in Fig. 6. The measuring bridge (bridge I) consists of two resistance boxes (R_1 and R_2 , both 10×100 ohm), a five-decades resistance box (R_3) and the measuring thermometer R_m . The controlling bridge (bridge II) contains the box (R_1), the measuring thermometer, the controlling thermometer and a five-decades resistance box (R_4). Both bridges are fed from the same lead accumulator via a Poggendorf circuit (resistance 20 ohms) permitting the application of the following voltages to the bridge 2, 1, and 0.7 V.

The two bridge signals are fed either to two totally separated amplifiers or to a motor-driven switch which connects alternatively the first or the second bridge to one and the same amplifier. When only one amplifier is used the output of the amplifier is also fed to a switch operating in phase with the input switch. Dead periods are included so as to prevent measuring signals from interfering with controlling signals or reverse. The switches operate at three complete cycles per second.

Both methods of amplification (one or two amplifiers) have been used. Amplification with two separate amplifiers showed to be somewhat advantageous.

The amplified measuring signal is fed to a commercial recorder. Since the output signal amounts to about 2 watt/degree, even recorders without amplification system may be adapted to the amplifier.

The amplified controlling signal (d.c.) is fed to the primary winding of a transformer. The secondary winding of this transformer is inserted in the circuit containing the heating element of the block. Consequently, when the controlling signal (d.c.) increases, the impedance in the circuit of the heating current (a.c.) decreases, thus causing an increase of the heating current. Reversely, a decrease of the controlling signal causes a decrease of the heating current, thus yielding a nice system of proportional control.

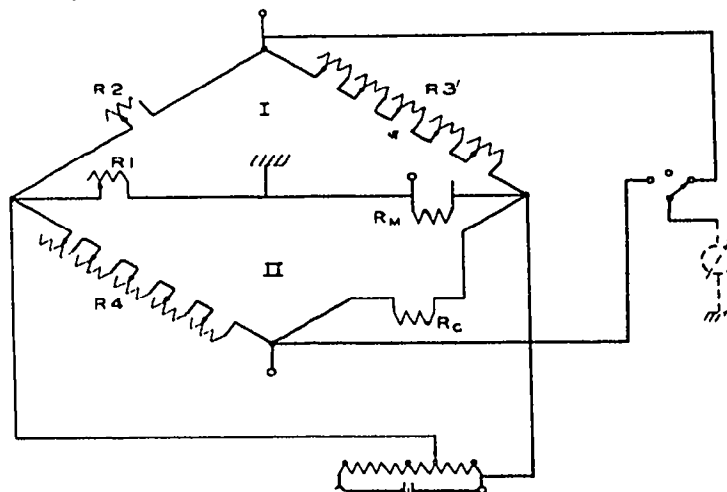


Fig. 6 Diagram of double Wheatstone bridge

The amplifier(s)

The d.c. signal coming from one of the bridges is fed to a chopper in order to convert d.c. into a c. After amplification the a.c. signal is again converted into a d.c. signal by a second chopper operating at the same frequency. The choppers are driven by the same synchronous motor. The frequency of the choppers is 40 hertz

The scheme of a double-purpose (switch-operated) amplifier is shown in Fig. 7

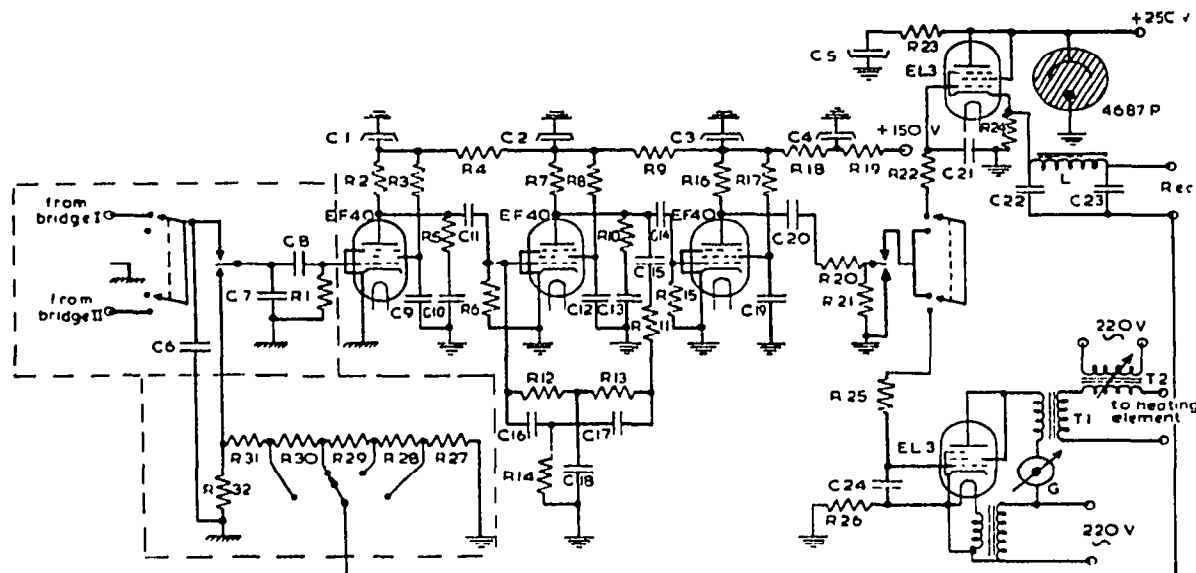


Fig 7 Scheme of microvolt amplifier, controlling and recording system

TABLE I

RESISTANCES AND CAPACITILS OBTAINING TO IIG 7

R 1	10 M Ω	R 12	115 K Ω	R 23	8 K Ω
R 2	15 M Ω	R 13	145 K Ω	R 24	33 K Ω
R 3	66 M Ω	R 14	47 Ω	R 25	470 K Ω
R 4	15 K Ω	R 15	10 M Ω	R 26	100 K Ω
R 5	220 K Ω	R 16	330 K Ω	R 27	1 Ω
R 6	10 M Ω	R 17	15 M Ω	R 28	4 Ω
R 7	15 M Ω	R 18	15 K Ω	R 29	5 Ω
R 8	66 M Ω	R 19	10 K Ω	R 30	90 Ω
R 9	15 K Ω	R 20	1 M Ω	R 31	400 Ω
R 10	220 K Ω	R 21	1 M Ω	R 32	1 Ω
R 11	330 K Ω	R 22	3 M Ω		
C 1	8 μ F	C 13	100 pF	L	10 henry
C 2	8 μ F	C 14	0.025 μ F		150 ohm
C 3	8 μ F	C 15	5000 pF	G	mA meter
C 4	8 μ F	C 16	26500 pF		separate
C 5	8 μ F	C 17	26500 pF		earthing
C 6	4 μ F	C 18	53500 pF		general
C 7	0.01 μ F	C 19	0.1 μ F		earthing
C 8	0.025 μ F	C 20	0.25 μ F		
C 9	0.1 μ F	C 21	0.1 μ F	Rec	recording
C 10	100 pF	C 22	16 μ F		mA meter
C 11	0.025 μ F	C 23	16 μ F		10 mA, 400
C 12	0.1 μ F	C 24	0.1 μ F		ohm

Since voltages as low as 10^{-6} are amplified, special attention has to be paid to shielding and earthing. The parts to be shielded have been enclosed in broken lines in the diagram. Two different symbols for earthing have been used indicating two separated earthing circuits. When no separate earthing is applied serious difficulties arise.

The choppers

The choppers (see Fig 8) used, are not unlike the one described by LISTON, QUINN, SARGEANT AND SCOTT⁴.

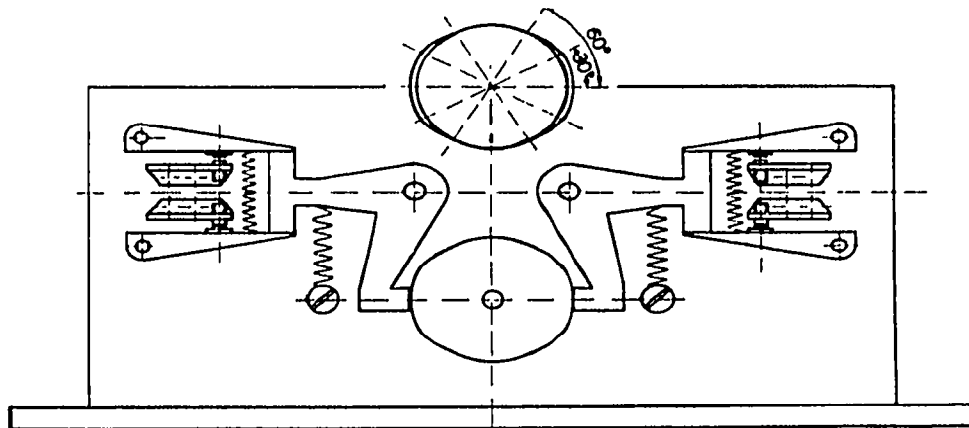


Fig 8 Chopper

The contacts are lifted by means of rotating discs driven by one and the same synchronous motor. The disc has a special shape (see insertion in Fig 8) in order to obtain a high speed of opening and closing of the contacts without causing large displacements of the contacts. This way of opening and closing contacts may have advantages over the method used by LISTON and coworkers; it reduces heat development and possible chattering.

Experimental details

The determination of a heating curve is carried out in the following way. The measuring vessel is filled with a weighed amount of substance. Usually quantities less than 500 mg are sufficient. The measuring thermometer is inserted into the measuring vessel containing the molten substance.

Care is taken that the sensitive part of the thermometer is at equal distance from the bottom and the inner wall of the measuring vessel. The level of the molten substance has to be about 2 mm above the top of the sensitive part of the thermometer. Eventually trapped air-bubbles are removed by gentle tapping. Then the substance is allowed to solidify and the measuring vessel with the thermometer is inserted in the block. The block is heated by switching the feeding transformer of the heating current to full.

The Wheatstone bridge contains a switch which connects the output of the bridge either to the input of the amplifier or to a mV-meter. By equilibrating the bridge on the mV-meter the temperature of the measuring vessel may be followed with an accuracy of about 1° .

When the measuring vessel has attained a desired temperature the heating is switched off and the block is allowed to equilibrate. The variable resistance of the controlling bridge is set on

$$R_4 = R_1 + R_c^\circ \alpha (T_2 - T_1)$$

where R_c° is the resistance of the controlling thermometer at zero degrees centigrade and $(T_2 - T_1)$ is the temperature difference to be maintained between the block and the measuring vessel*.

As a rule $(T_2 - T_1)$ is about 1.5°C , causing a rate of heating of about 0.3°C per minute.

The variable transformer feeding the heating element is adjusted to such a voltage that it can heat the block at a rate somewhat higher than desired. Provided the voltage is high enough, the setting of the variable transformer is not very critical since the controlling system may reduce the heating current by about 30% when the temperature of the block is only 0.03° high.

The amplifier(s) and the recorder are started and the apparatus records the heating curve. The sensitivity of the apparatus may be varied by means of a switch changing the back feed of the amplifier.

When the recorder shows full deflection, R_3 is increased by a distinct amount, *and the recording pen returns to near zero deflection*

The number of times R_3 has to be increased during a determination depends on the temperature range to be investigated and the sensitivity switched on. The sensitivity may be set so that a full scale deflection (10 cm) of the recorder corresponds with 0.12, 0.25, 0.40 or 3.5°C .

The apparatus shows a rapid response. When the voltage of the heating current is suddenly changed by about 25% the heating current is fully readjusted within 45 seconds. When the resistance R_3 is changed so that the recording pen travels over the full scale it attains its new final position within 40 seconds, whereas over 95% of the scale is travelled by the pen within one second.

The experience gained so far is restricted to temperatures between 20 and 200°C . In this range the apparatus operates quite satisfactory. Since the block is contained in a Dewar flask and may be easily cooled we see no objections to determinations at temperatures far below zero. (The measuring vessel shown is only a simple model. It may be easily changed in such a way that contact between the substance and surrounding air (moist) is prevented.) As a matter of fact, the apparatus is intended to be used both at high as well as at low temperatures.

ACKNOWLEDGEMENTS

We are much indebted to Mr W. SCHOON and Mr C. LANNING, glass-blower and instrument-maker at the Analytical Laboratory of the State University, Utrecht, for their skilful work in making resistance thermometers. Further thanks are due to Mr C. Z. VAN DOORN, Mr E. G. BERNIS and Mr C. C. V. D. SPOEL for their assistance during the development of this apparatus.

SUMMARY

A description is given of an apparatus for the determination of heating curves by means of the "thin film" method. The amount of substance used is about 500 mg. The apparatus permits the

* It is assumed that R_1 and R_2 are approximately equal to R_3 .

automatic recording of heating curves with an accuracy of 0.001°C within a range of 0.2°C . By simply resetting a resistance the next following range of 0.2°C may be recorded. Larger ranges may be investigated completely automatically, with a temperature sensitivity inversely proportional to the range, however.

The dimensions of the calorimetric part of the apparatus are discussed. The thermometers used are platinum resistance thermometers having a resistance of about 600 ohms at room temperature. The diameter of the thermometers is about 6.5 mm and their length amounts to 25 mm.

A scheme of the amplification system for recording the temperature and controlling the heating current is presented.

The apparatus may be used from temperatures of from 200°C to far below zero.

RÉSUMÉ

Un appareil pour la détermination des courbes de chauffage par la „méthode du film mince“ est décrit. La quantité de substance employée est de 500 mg. L'appareil permet l'enregistrement automatique des courbes de chauffage avec une précision de 0.001°C dans un intervalle de 0.2°C . En faisant changer simplement une résistance, on peut enregistrer l'intervalle de 0.2°C suivant. Des intervalles plus grands peuvent être étudiés automatiquement mais, la sensibilité à la température étant cependant inversement proportionnelle, à l'intervalle étudié.

Les dimensions de la partie calorimétrique de l'appareil sont discutées. Les thermomètres employés sont des thermomètres à résistance de platine avec une résistance de 600 ohms à température ordinaire. Le diamètre des thermomètres est de 6.5 mm environ, leur longueur de 25 mm.

Un schéma du système amplificateur pour l'enregistrement de la température et le réglage du courant de chauffage est présenté.

L'appareil peut être employé à des températures allant jusqu'à 200°C et jusqu'à bien en dessous de zéro.

ZUSAMMENFASSUNG

Ein Apparat zur Bestimmung von Erhitzungskurven mit Hilfe der „Dunnschichtmethode“ wird beschrieben. Die benutzte Substanzmenge betrug 500 mg. Der Apparat erlaubt die automatische Aufzeichnung von Erhitzungskurven mit einer Genauigkeit von 0.001°C in einem Bereiche von 0.2°C . Durch einfaches Verstellen eines Widerstandes kann der nächste Bereich von 0.2°C registriert werden. Größere Bereiche können vollautomatisch untersucht werden, wobei aber die Temperaturempfindlichkeit umgekehrt proportional dem Bereiche ist.

Die Dimensionen des kalorimetrischen Teiles des Apparates werden erörtert. Die benutzten Thermometer sind Platinwiderstand-Thermometer mit einem Widerstand von ungefähr 600 Ohm bei Zimmertemperatur. Der Durchmesser der Thermometer beträgt ungefähr 6.5 mm, die Länge 25 mm.

Ein Schema des Verstärkungssystems zur Temperaturregistrierung und Regelung des Heizstromes wird vorgelegt.

Der Apparat kann für Temperaturen bis zu 200°C und auch bis weit unter Null angewendet werden.

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Received April 18th 1957